

Effects of SEI on the Kinetics of Lithium Intercalation

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The successful operation of Li-ion cells is attributed mainly to the surface films on carbonaceous anode materials. These films provide the much-needed kinetic stability to the electrolyte species even at the thermodynamically reducing anode potential. Unlike the passive films on valve metals or in primary Li cells, the anode films in Li ion cells have moderate ionic conductivity and hence termed solid electrolyte interface.

Understandably, the performance of the anode is dictated largely by the characteristics of SEI, i.e., its resistance, ability to prevent further electrolyte reduction, amenability to charge transfer or Li intercalation process and to some extent the diffusivity of Li^+ ions, even though it is difficult to distinguish the slow diffusion across the SEI from the slow diffusional process within the bulk anode. The corresponding performance characteristics of Li-ion cells that would be affected by the SEI include cycle life, self-discharge, rate capability and low temperature. The characteristics of the SEI depend on several factors such as the nature of the carbonaceous material and electrolyte, temperature and mode of forming the SEI (rate and temperature).

Our recent research studies at JPL, have focussed on enhancing the low temperature performance of Li-ion cells, by a judicious selection of electrolyte, especially the solvent mixture. The characteristics of the SEI in the selected-solvent solutions have been determined in three-electrode cells by a variety of electrochemical techniques, such as ac impedance, DC micro polarization and Tafel polarization at various temperatures. These measurements have been supported by charge-discharge measurements at different temperatures and rates. For enhancing the low temperature performance, we have adopted the approach of initially optimizing the carbonate-based electrolytes, e.g., equi-proportion mixture of ethylene carbonate, dimethyl carbonate and diethyl carbonate¹ for achieving the desired SEI and later the use of quaternary additives, e.g., aliphatic esters such as methyl acetate, ethyl acetate, ethyl propionate and ethyl butyrate that have relatively poor filming properties, especially with low molecular weight esters and yet form highly conducting solutions at low temperatures (Fig. 1).² Also, we have used electrolyte additives, e.g., pyrocarbonates (Fig. 2),³ that would enable the formation of

suitable SEI. In all these studies, we have found that the interfacial properties are more critical than bulk ion migration processes in the electrolyte at low temperatures.

Acknowledgments

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References

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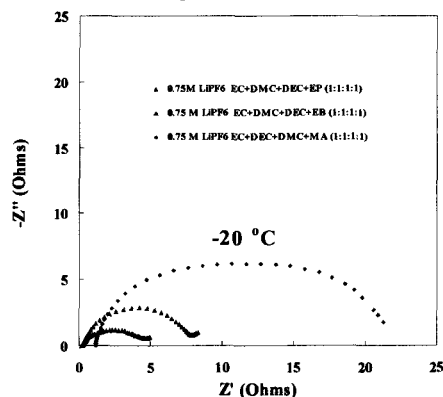


Fig. 1: EIS plots of graphite anode in solutions containing esters as quaternary solvent additive at -20°C .

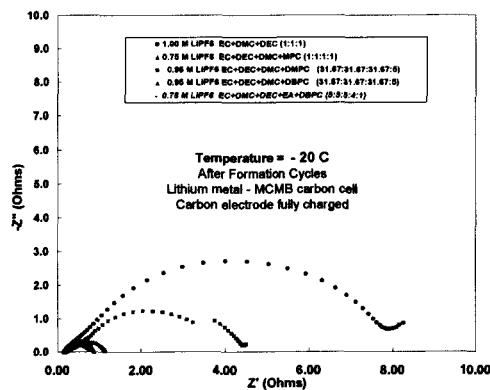


Fig. 2: EIS plots of graphite anode in solutions containing pyrocarbonate additives, dimethyl and dibutyl pyrocarbonates at -20°C .